INVESTIGATIONS OF MIXED POLYMER ELECTROLYTES BASED ON CASAVA STARCH AND SYNTHETIC POLYMERS FOR ENERGY STORAGE APPLICATIONS

A SYNOPSIS

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1. INTRODUCTION

The word ‘Polymer’ is a chemical compound derived from the Greek words ‘polus’ and ‘meros’, which refers to multiple times of repeating units in a molecules. A polymer can be classified as synthetic and natural polymers with unique properties. Even though synthetic polymers plays a vital role in real-time applications, their high cost, non-biodegradable and toxic nature to our environment limited their applications. As an alternative, naturally abundant, cost effective, biodegradable and ecofriendly natural polymers, like bio-polymers attracted a greater attention in recent times [1]. In recent days biopolymer is a one of the hottest field for the remedies of environmental issues towards an ecological future. Recent applications of biopolymers are, medicine, food packaging, textiles and energy storage devices. Naturally available bio-polymers are easily degradable and biocompatible materials, like, polysaccharides, protein and lipids from plant and animal resources. Polysaccharides are defined as repetition of large molecules of monosaccharides, such as fructose, galactose and glucose [2]. A starch is one of the polysaccharide materials available in natural and synthesised from plants. Generally, starch is abundant, biodegradable, inexpensive, cytocompatible and eco-friendly material on the earth. It consists of D-glucose unit linked by α-(1, 4) glucosidic bond and starch are made from plants in the form granules. The granular structure of starch contains partially crystalline phase and insoluble in cold water. Starch source are available from different plants, like rice, potato, corn and some citrus fruits. Cassava starch was obtained from Manihot esculenta crantz with tuberous roots from the family of Euphorbiaceae. Cassava starch has good film forming capacity due to high amylopectin and high viscosity content, low cost, high transparency and easily biodegradable nature [3]. For the purpose of energy storage application, biopolymer should possess certain requirements to fulfill the demand and it can be achieved by blending the biopolymer with synthetic polymers, which leads to blended biopolymers. Generally, addition of synthetic polymers lead to partial decomposition of materials, but the selection of polymers with biocompatible and less toxic nature can cause the decomposition easily by the micro-organism present in the environment in terms of di-degradable mechanisms, like compostable, photo-biodegradable, hydro-biodegradable and bio-erodible [4]. Similarly, synthetic biopolymers are degradable with the help of living organism or biotechnological process with long duration. The biocompatible synthetic polymers are, Polylactic acid (PLA), polyvinyl alcohol (PVA), polyhydroxy-

butyrate (PHB), and polyglycolic acid (PGA). Blended biopolymer has unique chemical and physical properties in energy storage applications in the form of polymer electrolyte membrane with better results in our day to day life.

Nowadays, to save energy due to lacking of fossil fuels and climate change caused by exhaustion of fossil fuel reserve, requires energy storage systems [5]. The limited source of fossil fuels and increasing population has motivated the researchers to develop the new energy conversion and storage technologies from the renewable resources. Electrochemical energy storage devices store the electrical and chemical form of energies. The common electrochemical energy storage devices are capacitors, batteries, fuel cells, supercapacitors and electro-chromic devices [6]. The electrical storage systems need to store charges for a longer period of time. But the starting device of battery or fuel cells are lacking behind on these requirements due to limited specific energy and specific power with discharging time [7]. For example, capacitors having high power density, but their energy density is low. As the same, supercapacitors having high power density, but are not capable for high energy density. Generally, there are three types of supercapacitors namely, i) electric double layer capacitors, ii) Pseudocapacitors and iii) hybrid capacitors. Supercapacitor device generally consist of two carbon electrodes, which are sandwiched by the biopolymer electrolyte [8]. Since, the biomass wastes (such as leaves, roots, seed, and fruit starch etc.,) are the rich sources of carbon, they are suitable for preparing the carbon material. It can provide better device performances, like high energy density, long term operating stability, low cost, high reliability and eco-friendly [9]. In this work, biopolymer electrolyte and biomass derived carbon materials are used for energy storage purposes as an alternative source for synthetics and metal oxide materials.

2. LITERATURE REVIEW

An electrolyte was acted as a charge transfer medium for electrochemical devices, which allowed the flow of ions between the cathode and anode. Polymer electrolyte performances were evaluated by their ionic conductivity and ion transport properties, which were depending on the mobility of polymer chains, degree of salt dissociation, dielectric constant of the polymer host and degrees of ion aggregation [10]. The first electrolyte of semi-synthetic polymer was produced by Bakelite in 1909 and synthetic polymer electrolyte in 1911. The synthetic materials have some

drawbacks, like global warming, shortage of petroleum, high cost and not environmental friendly. Biopolymer electrolyte from natural and biomass polysaccharides, such as pectin, cellulose, chitosan and starch, were the alternatives to the synthetic materials. Even though, starch was a naturally abundant material, with low cost, biodegradable and eco-friendly nature, their applications were limited by their hydrophilicity and brittleness. Polymer blending with some semi-synthetic polymers was the only solution to overcome these problems. Addition of salt and fillers were also used to improve the performance of the electrolyte [11].

Zhu [3] reported the characteristics of cassava starch, such as composition, physical and chemical structures, physicochemical properties and nutritional quality. They proposed that the low cost, large and sustainable supply of cassava starch provides an excellent basis for diverse applications, such as food packaging, textile and energy storage devices.

Zahid et al [12] reported that cassava starch as gel polymer electrolyte for zinc air battery. Cassava powder mixed with deionised water before heated to gelling form and then mixed with KOH at different concentration to form gel polymer electrolyte. The electrolyte was characterized by ionic conductivity, viscoelastic and window stability.

Arrieta et al [13] reported the synthesis and characterization of biofilms using cassava starch with different amounts of glycerine, glutaraldehyde, polyethyleneglycol and lithium perchlorate. The prepared this film were characterized by electrical impedance spectroscopy, scanning electron microscopy, attenuated total reflectance-Fourier transform infrared spectroscopy and thermogravimetric analyses.

Jothi et al [14] reported the electrochemical characteristics of corn starch blended PVP with various composition of NH_4Br based polymer electrolyte by using solution casting technique. Among the various prepared samples, CPN-30 revealed the higher ionic conductivity of 1.31×10^{-4} S/cm. The amorphous nature and increments of ions using de-convolution technique was obtained from XRD and FTIR analyses. Cyclic voltammetry study for higher ionic conductivity sample showed the faradaic pseudocapacitive behaviour. The have fabricated a proton conducting cell using the prepared sample and it showed the open circuit potential of 1.24V.

Marf et al [15] reported the electrochemical characteristics of PVA:Chitosan blend polymer electrolyte with plasticizer as the proton conducting electrolyte. The ionic conductivity of the proposed polymer electrolyte was found to be 1.39×10^{-4} S/cm and the prepared sample with higher ionic conductivity was utilized for device fabrication. The fabricated device were characterised by CV study and it revealed the EDLC behaviour with rectangular shaped CV curves. They have concluded that the fabricated device revealed the specific capacitance of 39 F/g at first cycle and it was reduced to 19 F/g at the end of 250 cycles. Similarly, the power density value was 380 W/kg at first cycle and stable at 90 W/kg up to 250 cycles.

Ponmani et al [16] reported the electrochemical studies of solid polymer electrolytes based on PVDF-HFP/PVAc:Mg $(ClO_4)_2$ for Mg ion batteries. The showed that the prepared polymer electrolyte exhibited the higher ionic conductivity of 2.93×10^{-4} S/cm at 363K. Also, the cyclic stability window of higher conductive electrolyte was 4V.

Lee et al [17] reported the possibility of utilizing coconut shell derived activated carbon for high performance of solid state supercapacitors. They have prepared activated carbon by hydrothermal method from the coconut shell. The fabricated device using the prepared activated carbon showed the highest specific capacitance of 88 Fg^{-1} with the energy density value of 48.9 $Whkg^{-1}$. Also, the fabricated electrochemical device showed 92% of capacitance retention at 2 Ag^{-1} by the end of 5000 cycles.

3. OBJECTIVES OF THE RESEARCH WORK

The objective of this work was to study the role of cassava starch mixed synthetic polymers as a bio-polymer electrolyte in energy storage applications. In this process, different concentration of ammonium and magnesium nitrate salts were used as the donors to improve their ionic conductivity. Finally, EDLC devices were fabricated based on the better performed electrolytes and characterized. The objectives of the proposed research work was achieved through the following steps.

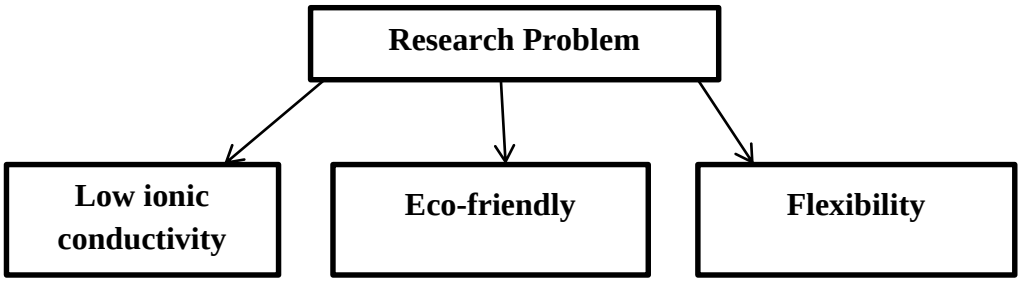
- Literature review on cassava starch based bio-polymer electrolyte was done to prepare biopolymer electrolyte membrane for energy storage devices
- Cassava starch blended with synthetic polymers (PVP, PVA) were prepared with various concentration of ceric ammonium nitrate

- ❖ Mixed bio-polymer electrolytes of cassava starch and PVDFHFP with various concentrations of magnesium nitrate were prepared
- ❖ Bio-mass derived carbon from jack fruit seeds were prepared and used as the bio-filler to improve the electrochemical performances of the mixed bio-polymer electrolytes (cassava starch and PVDFHFP based mixed polymers with various concentration of magnesium nitrate)
- ❖ The prepared biopolymer electrolyte were characterized by XRD, FTIR, SEM, TGA, AC impedance and electrochemical (CV, LSV and GCD) techniques.
- ❖ The prepared electrolytes with superior ionic conductivities were used to fabricate the EDLC devices and their performances were studied by using rGO and activated carbon as the electrode materials.

4. RESEARCH PROBLEM

The fundamental requirement of polymer electrolytes for energy storage devices were high ionic mobility, high electrochemical stability, flexibility and environmental friendliness. But most of the solid polymer electrolyte possessed poor ionic conductivity and stability, which limited their role in energy storage devices. Also, most of the solid polymer electrolytes were made up of synthetic polymers, like, PVA, PVP, PVDF, etc., and synthetic polymers were well known for their semi-crystalline and toxicity, which affected their ionic conductivity and performances. To attain higher conductivity and stability, synthetic polymers were blended with bio-polymers. When the bio-polymers were blended with synthetic polymers, it increased the degradability and eco-friendliness of the synthetic polymers. Similarly, the conductivity of the polymers/ blended polymers were improved by the addition of inorganic salts, plasticizers, ionic liquid or filler, with the existing bio-polymers. In terms of fillers, metal oxides like, Al_2O_3, SiO_2, TiO_2 and V_2O_5 were used in polymer electrolytes. But, the toxicity of these metal oxides urged the researchers to develop alternate fillers with eco-friendly nature for this purpose. As an alternative, materials derived from the bio-wastes, like coconut shell, fruit seed wastes, leaves, etc., were used as the fillers. These biomass derived materials were easily degradable, low cost and less and/or non-toxic to the environment. Mixed bio-polymers (based on bio-polymers and synthetic polymers) loaded with inorganic salts and/or bio-fillers, opened a new gate way for the

preparation of highly stable and efficient solid state electrolyte for energy storage applications.



5. ORGANIZATION OF THESIS

In this work, mixed bio-polymers with cassava starch and synthetic polymers were investigated as a stable solid state electrolyte. The ionic conductivity and stability of the prepared electrolytes were improved by the addition of inorganic salts (ammonium ceric nitrate and magnesium nitrate) and bio-fillers (biomass derived carbon from jack fruit seeds). The prepared bio-polymer electrolytes were analytically characterized and their electrochemical characteristics were investigated through the fabrication of EDLC devices. The proposed work was executed and reported in eight chapters.

Chapter1 discussed the introduction of biopolymer electrolytes and their role in energy storage devices. Biopolymers are classified into various types based on their nature, availability and synthesis methods. Different types of polymer electrolytes, such as, solid electrolyte, blend electrolyte, gel electrolyte and composite electrolyte, and their role in energy storage devices were discussed. Preparation of polymer electrolyte, blending and their advantages were discussed. Finally, the necessity of mixed bio-polymer electrolytes and their property enrichments were pointed out.

Chapter 2 described the literature review of the reported work. This chapter briefly explained the recent advancements in polymer and bio-polymer electrolytes. The electrochemical performances of the synthetic polymer electrolytes were explained. The performances of the blend polymer and cassava starch based bio-polymer electrolytes were discussed. Literatures related to the performance enhancement by ceric ammonium nitrate and magnesium nitrate based salts were reviewed and discussed. Also, the role of bio-fillers and their necessity in bio-polymer

electrolytes were discussed. Based on the literature, the research gap was identified and the scope of the work was framed.

Chapter 3 deals with the materials required, preparation techniques and characterization techniques of the reported research work. The precursors utilized for the preparation of mixed bio-polymer electrolytes were listed with purity. General synthesis techniques of bio-polymer electrolyte were discussed with the detailed explanation about solution casting technique. The characterization techniques, such as, X-ray Diffraction analysis (XRD), Fourier Transform Infra-Red (FTIR) spectroscopy, AC impedance (cole-cole plot, conductance spectra, dielectric analysis, tangent spectra) spectroscopy, Scanning Electron Microscopy (SEM), and Thermo Gravimetric Analysis (TGA), utilization for the analysis of the prepared samples, were discussed with specification and working mechanisms. EDLC device fabrication procedures and their evaluation, using CV and GCD analyses were described.

Chapter 4 deals with the synthesis and characterization of biodegradable solid blend polymer electrolytes based on cassava starch and synthetic polymer Poly [vinyl pyrrolidone] (PVP) with a constant amount of Ammonium ceric nitrate $[(NH_4)_2\mathrm{Ce}(NO_3)_6]$. The Biopolymer starch is used to enhance the biodegradability of the polymer membranes. Preparation of blend polymer electrolytes by solution casting method using deionized water as solvent were discussed. The physical and chemical characteristics of the prepared electrolytes are analyzed with structural, vibrational, electrical and electrochemical behavior by using different characterization techniques. The ionic conductivity and dielectric measurement of the electrolytes were carried out by the impedance spectroscopy techniques. The maximum ionic conductivity of 8.1×10^{-6} S/cm was measured at room temperature for 80% PVP: 20% cassava starch: 2% ammonium ceric nitrate (ACN) blended system. The dielectric properties of the prepared polymer electrolytes were also analyzed. The electrochemical characteristics of the prepared higher ionic conductivity sample was tested with cyclic voltammetry (CV) and linear sweep voltammetry (LSV) techniques. The observed electrochemical properties were described.

Chapter 5 described the electrochemical characteristics of polyvinyl alcohol (PVA)/cassava starch (CS) based blend polymer electrolyte with ammonium ceric nitrate. The role of PVA and ammonium ceric nitrate on the structural characteristics

of the cassava starch were studied by XRD analysis. The interactions between the ammonium ceric nitrate and polymer blend was studied by the FTIR analysis. The thermal behavior of the prepared solid polymer electrolyte between 30˚ and 500˚C were examined by the TGA at nitrogen atmosphere. The surface morphology and elemental compositions of the prepared blend polymer electrolyte were examined by the SEM and EDAX analyses. The impedance spectroscopy technique was used to measure the ionic conductivity values in the frequency range of 42 Hz – 1MHz at room temperature. The maximum ionic conductivity of 1.53×10^{-5} S/cm was observed for 2% ammonium ceric nitrate loaded blend polymer. The electrochemical studies revealed that the prepared blend polymer electrolyte possessed Electric double layer capacitance through non-faradaic behavior. Linear sweep voltammetry analysis suggested that the prepared higher ionic conductivity electrolyte possessed the extended potential window of -2V to +2V. Prepared blend polymer electrolyte exhibited the specific capacitance value of 16 Fg^{-1} 25 mV/s^{-1}.

Chapter 6 reported the electrochemical characteristics of cassava starch mixed PVDF-HFP polymer electrolyte with different amount of magnesium nitrate salts. Mixed polymer electrolyte was prepared by solution casting technique and characterized by XRD, FT-IR, SEM, EDAX and impedance spectroscopy analyses. The X-ray diffraction analysis confirmed increased amorphous nature of the prepared polymer electrolytes. Impedance spectroscopy results proved that the prepared polymer electrolyte with 15% magnesium nitrate loading showed superior ionic conductivity at ambient temperature. Thermal stability of the prepared polymer electrolyte was studied by the TG analysis within the temperature range of room temperature to 600˚C. Electrochemical measurements were performed for higher conducting electrolytes and it showed the pseudo-capacitive nature with oxidation and reduction peaks within the potential window of -0.5 to 0.4V. The electrochemical measurements suggested that the prepared mixed polymer electrolyte was suitable for energy storage applications.

Chapter 7 described the role of biomass derived carbon as activated carbon and bio-filler on the electrochemical performances of the magnesium nitrate loaded cassava starch/ PVDF-HFP blend polymer electrolyte. In this work, biomass derived carbon from jack fruit seeds were utilized as the bio-fillers, as an alternative to the synthetic fillers or plasticizers. Also, it was used as the activated carbon for the fabrication of

EDLC devices. Bio-filler (carbon from jack fruit seeds) based electrolytes were prepared by cassava starch/PVDF-HFP/$MgNO_3$ with various concentrations of filler by using solution casting technique. The prepared electrolyte and biosynthesized filler concentration were optimized by the semi-crystalline and amorphous phase of bio-filler and polymer electrolytes. Prepared bio-filler based blend polymer electrolyte were studied by the FT-IR and SEM analyses. The thermal stability and degradation of the prepared polymer electrolyte was studied by TGA/DTG and DSC analyses within the temperature range of 30 – 600 °C. The highest ionic conductivity of 2.166×10^{-4} S/cm was achieved by the incorporation of bio-filler to the existing cassava starch/PVDF-HFP blend polymer and it was significantly higher than that of synthetic fillers based polymers. Arrhenius behavior of the prepared electrolyte was identified by the temperature dependent conductivity and dielectric studies. Finally, EDLC devices were fabricated using the biomass derived carbon as the activated carbon and their performances were tested using the prepared bio-filler based blend polymer electrolyte. The fabricated device showed superior CV and GCD performances within the potential window of -2V to 2V.

Chapter 8 described the overall summary and conclusion of the reported research work. Biodegradable polymers of cassava starch blended with various synthetic polymers like PVP, PVA and PVDFHFP were synthesized using solution casting technique. The ionic conductivity of the prepared blend polymer electrolytes was improved by the incorporation of inorganic salts (such as ceric ammonium nitrate and magnesium nitrate). Further, the role of biomass derived carbon as the bio-filler on the electrochemical performances of the Casava starch/PVDFHFP/ Magnesium nitrate blend polymer electrolyte. The electrochemical performances of the prepared higher conductivity electrolytes were tested through the fabrication of EDLC devices. Based on the results, the suggestions for the future work is reported.

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7. List of Publications

1. **C. Nithya Priya,** R. Muruganandham, M. Muthuvinayagam, and M. Vahini, "Studies on pectin-polyvinyl alcohol-based biodegradable polymer blend electrolytes," Mater. Perform. Charact., vol. 9, no. 1, pp. 692–700, 2020, doi: 10.1520/MPC20200095. (scopus with 0.7 imp)
2. **C. Nithya Priya,** M. Muthuvinayagam, S. Ramesh, and K. Ramesh, "Studies on structural, electrical and electrochemical properties of biodegradable PVP/starch blend polymer electrolytes with ammonium ceric nitrate for energy storage devices," Energy Environ., pp. 1–18, 2022, doi: 10.1177/0958305X221116174. (3.1 imp)
3. **C. Nithya Priya,** M. Muthuvinayagam & M. Vahini Environmental friendly solid blend polymer electrolytes based on PVA:starch:ceric ammonium nitrate for electric double layer capacitor (EDLC) applications, Journal of Materials Science volume 58, pages773–786 (2023). (4.6 imp).
4. **Nithya Priya C,** Muthuvinayagam M, Arivarasan A, Balasubramani V, Eco-friendly starch based Mg^{2+} ion conducting polymer blend electrolytes for electrochemical device applications, Journal of Materials Chemistry and Physics, 2023, Accepted.